

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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To:

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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing
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07.04.2006

Applicant's or agent's file reference
2003B138

IMPORTANT NOTIFICATION

International application No.
PCT/EP2004/014479

International filing date (day/month/year)
16.12.2004

Priority date (day/month/year)
18.12.2003

Applicant
EXXONMOBIL CHEMICAL PATENTS INC.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

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11 APR 2006

Name and mailing address of the international preliminary examining authority:



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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2003B138	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/EP2004/014479	International filing date (day/month/year) 16.12.2004	Priority date (day/month/year) 18.12.2003	
International Patent Classification (IPC) or national classification and IPC INV. C07C29/141 C07C29/17 C07C45/50 C07C45/74 C07C11/02			
Applicant EXXONMOBIL CHEMICAL PATENTS INC.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 7 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 18.10.2005		Date of completion of this report 07.04.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized officer Kardinal, S Telephone No. +31 70 340-3483	



INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/014479

AP20 Rec'd PCT/PTO 13 JUN 2006

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-38 as originally filed

Claims, Numbers

1-45 received on 18.10.2005 with letter of 18.10.2005

Drawings, Sheets

1/1 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
 4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/014479

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-41
	No: Claims	42-45
Inventive step (IS)	Yes: Claims	
	No: Claims	1-45
Industrial applicability (IA)	Yes: Claims	1-45
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

PCT/EP2004/014479

Re Item V**Reasoned statement with regard to novelty and inventive step; citations and explanations supporting such statement****1. Reference is made to the following documents :**

- D1: US 2003/114718 A1 (BUSCHKEN WILFRIED ET AL) 19 June 2003
- D2: US-A-4 684 750 (ZGORZELSKI WOLFGANG ET AL) 4 August 1987
- D3: WO 02/094740 A (MCMATH SARAH ELIZABETH JANE ; ANDERSON KRIS (GB); GOODRICH PETER (GB);) 28 November 2002
- D4: GB 643 503 A (N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 20 September 1950
- D5: US-A-5 324 420 (DE MUNCK ET AL) 28 June 1994

2. Novelty and Inventive Step

2.1 Document D1 discloses (cf. the passages indicated in the international search report) a process for the production of alcohols by hydroformylation and catalytic hydrogenation in the presence of water which is dissolved in the homogeneous liquid hydrogenation mixture such that no additional liquid water phase is present under reaction conditions. The process according to D1 aims to improve the yield in alcohol by hydrolysing by-products such as acetals, formates and aldol products and convert them into the target product.

In a preferred embodiment of the process according to D1 (cf. paragraph 46 and 49) a plurality of reactors is used in series while adding water before the individual reactors.

The process according to claim 1 differs from this known production of alcohols in that the material fed to the first hydrogenation reactor has a sulphur content of below 10 ppm by weight.

The subject-matter of independent claim 1 and dependent claims 2-41 is therefore novel (Article 33(2) PCT).

2.2 D1 can be considered as representing the closest prior art to the subject-matter of claim 1.

Technical effects that could result from controlling the sulphur content of the material fed to the first hydrogenation reactor (which is influenced by the sulphur content of the starting olefin, the syngas and other components used in the hydroformylation reaction) include avoiding adverse effects on the catalyst performance (if the catalyst is poisoned by sulphur-containing compounds) and reducing the sulphur content of the final products.

However, the process of claim 1 is not limited with regard to the nature of the hydrogenation catalyst and encompasses the use of catalysts which are not sensitive to sulphur (e. g. the known Mo oxide catalysts). The only technical effect remaining for the whole scope of claim 1 is therefore a reduced amount of sulphur in the target products.

The objective technical problem may therefore be formulated reducing the amount of contaminants in the target products.

The solution proposed in claim 1 of the present application cannot be considered as involving an inventive step (Article 33(3) PCT) for the following reasons :

The skilled person would expect to obtain purer target products from less contaminated starting materials and it has to be regarded as obvious to use starting materials, including both the olefins and the syngas, having a low content of impurities (such as sulphur compounds, see D5, column 1, lines 11-22) in order to obtain purer target alcohols.

The definition of a certain desired purity of the material fed into the hydrogenation reactor can therefore not be considered as involving an inventive step.

2.3 It is furthermore known, that sulfur compounds are catalyst poisons (see for instance D5), and for syntheses, particularly those using sensitive catalysts, it is

obvious to use educts, including syngas, having a low sulphur concentration in order to prolong the catalyst life.

The aldolisation of hydroformylation products is a standard procedure to generate higher, branched products (cf. e. g. D2) and the skilled person would include such an aldolisation step in a process according to D1 if desired. The use of ionic liquids in hydrogenation processes is known from D3. The hydroformylation in two reactors and the recycling of unreacted gases from the hydroformylation and the subsequent hydrogenation is known from D4.

It has to be regarded as belonging to the routine work of the skilled person to include these features into the aforementioned processes. Dependent claims 2-41 do not seem to contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step.

2.4 The document D1 discloses (cf. paragraph 33) several methyl heptenes and the mixture of isomeric C8-olefins obtained in the dimerisation of butene (dibutene). Such mixtures are generally predominantly branched. D1 furthermore discloses (cf. example 1) a mixture of C9 aldehydes, suitable for use as hydrogenation feed stream for the production of C9 alcohols. The purity of these mixtures with respect to sulphur or chlorine is not disclosed.

However, a specific degree of chemical purity of low molecular compounds or mixtures thereof does not constitute a new element imparting novelty to the claimed subject-matter. A document disclosing such compounds or mixtures makes these available to the public within the meaning of Art. 33 (2) PCT in all grades of purity as desired by a person skilled in the art.

The subject-matter of claims 42 to 45 is therefore not novel (Article 33(2) PCT).

It is furthermore generally known that chlorine and sulphur are potential catalyst poisons (cf. D5) and it would have to be considered as obvious for the skilled person to provide an olefin or aldehyde feedstock low in these contaminants in order to prolong the catalyst life if necessary.

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CLAIMS

1. A process for the production of alcohols comprising the hydroformylation of an olefin or olefin mixture followed by catalytic hydrogenation, wherein the hydrogenation is performed in a series of at least two reactors and water is added to the material discharged from the first reactor that is to be hydrogenated in the second reactor, in an amount such that in the second reactor, all the water present is dissolved in the organic phase and wherein the material fed to the first hydrogenation reactor has a sulphur content of below 10 ppm by weight.
2. A process according to claim 1 wherein water is added to the hydroformylation reactor, no further water is added in the first hydrogenation reactor and water is added to the second hydrogenation reactor.
3. The process according to claim 1 or 2 in which water is carried over from the hydroformylation reactor or a demetalling or washing step downstream of the hydroformylation reactor, into the first hydrogenation reactor, the amount of water carried over being such that all the water present in the first hydrogenation reactor is dissolved in the organic phase to be hydrogenated in the first hydrogenation reactor.
4. The process according to claim 3 in which further water is added to the material entering the second hydrogenation reactor, the amount of water added being such that all the water present in the second reactor is dissolved in the organic phase to be hydrogenated therein.
5. The process according to any of the preceding claims in which the sulphur content of the feed to the first hydrogenation reactor is below 5 wt. ppm.

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6. The process according to any of the preceding claims in which the olefin or olefin mixture used for hydroformylation has a sulphur content below 10 wt. ppm, preferably below 5 ppm, more preferably below 1 ppm.
7. The process according to any of the preceding claims in which the chlorine content of the feed to the first hydrogenation reactor is below 10 wt. ppm, preferably below 5 ppm.
8. The process according to any of the preceding claims for the production of C_6 to C_{15} alcohols from C_5 to C_{14} olefins or olefin mixtures.
9. The process according to any of the preceding claims in which the hydroformylation is performed at elevated temperatures and pressures using a cobalt catalyst.
10. The process according to claim 9 in which cobalt species are removed from the product of hydroformylation prior to hydrogenation in the first hydrogenation reactor.
11. The process according to claim 9 or 10 in which the product of hydroformylation is treated to remove cobalt species so that the cobalt content is below 2 wt. ppm prior to hydrogenation.
12. The process according to any of the preceding claims in which the hydroformylation is performed at pressures from 50 to 350 barg, preferably 150 to 350 barg, most preferably from 275 to 325 barg and temperatures from 165 to 185°C preferably from 170 to 180°C.
13. The process according to any of the preceding claims in which the hydroformylation reaction is performed in a series of at least two reactors.

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14. The process according to any of the preceding claims in which the gas composition in the hydroformylation reactor(s) is controlled by recycle of unreacted gasses from hydroformylation.

15. The process according to claim 13 or 14 wherein the hydrogen level in the second (and any subsequent) hydroformylation reactor(s) is replenished by balancing the composition of recycle gasses and/or by introducing unreacted gasses from the downstream hydrogenation reactor used to convert aldehydes in the final product of hydroformylation into alcohols.

16. The process according to claim 13, 14 or 15 in which a series of at least three hydroformylation reactors is used, and a hydrogen rich gas, comprising recycle gas from the hydroformylation reaction and/or from the downstream hydrogenation section, is fed to the third reactor.

17. The process according to any of the preceding claims in which the hydroformylation catalyst is cobalt and cobalt catalyst species are removed by injection of base such as caustic soda and/or sodium carbonate into the reaction product in a decobalter vessel following the final hydroformylation reactor.

18. The process according to claim 1 or 2 further comprising the aldolisation of at least a portion of the aldehyde or aldehyde mixture produced in hydroformylation, and catalytic hydrogenation of at least a portion of the aldolisation product.

19. The process according to claim 18 in which water is carried over from the aldolisation reactor into the first hydrogenation reactor, the amount of water carried over being such that all the water present in the first hydrogenation reactor is dissolved in the organic phase to be hydrogenated in the first hydrogenation reactor.

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20. The process according to claim 19 in which further water is added to the material entering the second hydrogenation reactor, the amount of water added being such that all the water present in the second reactor is dissolved in the organic phase to be hydrogenated therein.

21. The process according to any of claims 18 to 20 wherein the olefin or olefin mixtures comprises C₂ to C₄ olefins.

22. The process according to claim 21 using rhodium hydroformylation catalyst.

23. The process according to claim 21 or 22 using a phosphorus ligand in its hydroformylation reactor.

24. The process according to claim 23 wherein the phosphorus ligand is triphenylphosphine.

25. The process according to claim 23 wherein the phosphorus ligand is an organic phosphite.

26. The process according to claim 25 wherein the organic phosphite is 6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylethyl)-1,1'-biphenyl]-2,2'-diyl] bis(oxy)] bis-dibenzo [d,f] [1,3,2]-dioxaphosphin.

27. The process according to any of claims 21 to 26 wherein a C₈ alcohol is produced from propylene.

28. The process according to any of claim 21 to 26 wherein a C₉ alcohol is produced from ethylene.

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29. The process according to any of claims 21 to 26 wherein a C₁₀ alcohol or alcohol mixture is produced from butene or from a butene mixture.

30. The process according to any of the preceding claims in which the hydrogenation catalyst is a cuprous chrome catalyst.

31. The process according to claim 30 in which the hydrogenation catalyst contains from 20% to 40% by weight of each of copper and chromium based on the total weight of hydrogenation catalyst including any support, preferably from 25% to 35% of each of copper and chromium, more preferably from 28% to 32% of each of copper and chromium, most preferably 29% to 31% of each of copper and chromium.

32. The process according to any of claims 1 to 29 in which the hydrogenation catalyst comprises a monometallic or bimetallic or trimetallic catalyst composition on a solid support.

33. The process according to claim 32 wherein the support is selected from alumina or silica-alumina or a carbonaceous support.

34. The process according to claim 33 wherein the catalyst composition further comprises an acidity modifier.

35. The process according to claim 34 wherein the acidity modifier comprises a member of Group IA or IIA of the Periodic Table of the Elements.

36. The process according to claim 35 wherein the acidity modifier comprises magnesium, sodium or potassium, or a compound containing magnesium, sodium or potassium.

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37. The process according to any of claims 1 to 29 in which the catalytic hydrogenation uses a transition metal hydrogenation catalyst dissolved in an ionic liquid.

38. The process according to claim 37 wherein the transition metal is selected from nickel, cobalt, copper, palladium, chromium, ruthenium and rhodium, or a mixture of any two or more thereof.

39. The process according to claim 37 or 38 wherein the ionic liquid comprises in combination a first component selected from $[\text{BF}_4]^-$, halide anions, $[\text{PF}_6]^-$, $[\text{CF}_3\text{COO}]^-$, and $[\text{SbF}_6]^-$, and a second component selected from $[\text{emim}]^+$, $[\text{bmim}]^+$, any other disubstituted immedazolium, the substituents being C1-C4 alkyl, or $[\text{NBuPy}]^+$ or another suitable alkylammonium cation.

40. The process according to any of the preceding claims in which the product from the first hydrogenation reactor passes in a line to the second hydrogenation reactor and water is injected into the line and the mixture passes to a mixer whereby the water and the product are mixed so that the water is dissolved and/or entrained in the product, and the mixture is then passed to the second hydrogenation reactor where it passes through a catalyst bed at a temperature of 170 to 190°C at a hydrogen pressure of 40 to 200 barg.

41. The process according to claim 40 in which from 1 to 2 wt % of water based on the weight of organic material is injected.

42. A mixture of C_5 to C_{13} olefins comprising at most 90 mol % of normal olefins, which mixture is useful in the production of alcohols by hydroformylation of the olefin mixture followed by hydrogenation, said olefin mixture containing below 1 ppm sulphur by weight, preferably below 0.1 ppm, and below 1 ppm chlorine by weight, preferably below 0.1 ppm.

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43. The olefin mixture according to claim 42 wherein more than 50 wt. % of the mixture comprises C₈ olefins.

44. A hydrogenation feed stream comprising aldehydes containing from 6 to 15 carbon atoms useful in the production of alcohols by hydrogenation, said hydrogenation feed stream containing no more than 10 wt. ppm, preferably no more than 5 ppm and more preferably no more than 1 ppm, most preferably below 0.1 ppm, sulphur and no more than 10 wt. ppm, preferably no more than 5 ppm, and more preferably no more than 1 ppm, most preferably below 0.1 ppm chlorine.

45. The hydrogenation feed stream according to claim 44 comprising aldehydes containing nine carbon atoms, useful in the production of C₉ alcohols.

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